Final exam items
MSc in Chemistry
University of Pécs, Faculty of Science

Note: the candidate selects two of the four topics at random and draws 1-1 items from the topics. The details include the areas that the student is expected to explicate. Additional questions may arise during the exam.

TOPIC 1. INORGANIC CHEMISTRY

1. Describe the most important inorganic compounds of alkali and alkaline earth metals, their organometallic derivatives and bio-inorganic, chemically significant complexes. *(hydrides, halides, oxygen-containing derivatives; complexes with crown ethers and cryptands, as well as biologically important multidentate ligands; alkaline earth metal organics and their synthetic applications)*

2. Describe the most important inorganic compounds of boron and aluminum, and their organic derivatives. *(hydrides, halides, oxygen-containing derivatives; organoboron compounds and their synthetic applications; synthesis of organoaluminum compounds and their practical applications)*

3. Describe the most important inorganic compounds of silicon, tin and lead, and their organic derivatives. *(hydrides, halides, oxygen-containing derivatives, silicates; organosilicon derivatives of practical importance; synthesis of organotin compounds and their application in catalysis; lead derivatives, lead binding in biological systems)*

4. Describe the oxygen-containing compounds of nitrogen, phosphorus and arsenic. How are nitrogen and phosphorus incorporated into biological systems? *(oxygen compounds, complexes, oxoacids; important esters of oxoacids; nitrogen fixation in biological systems; phosphanes, phosphites as ligands in transition metal complexes)*

5. Describe the oxygen, sulfur and selenium compounds as well as compounds of practical interest. *(derivatives formed with hydrogen; oxoacids, esters; strength of acids; incorporation of elements into biological systems; oxygen complexes, organoselenium derivatives)*

6. Compare halogens and their compounds in terms of their redox reactions! Describe the significant fluorine and iodine compounds. *(halides, interhalogens, oxoacids; the role of chloride ion in biological systems; iodine-containing compounds possessing hormone action)*

7. Describe the most important complexes of the titanium and vanadium and their practical (catalytic) application. *(oxides, hydrides, organometallic derivatives; complexes containing organic and inorganic ligands; practical applications)*

8. Describe the compounds of the chromium group elements. *(halides, oxygen-containing derivatives; iso- and heteropolyacids; their carbonyl, alkylidene, alkylidine complexes; complexes with neutral organic ligands)*

9. Describe the most important complexes of the elements of the iron group, and their biocoordination chemistry. *(halogen, carbonyl, phosphane complexes; hydrogen derivatives; heme and heme proteins; enzymes; vitamin B12)*

10. Describe platinum metals. Describe some organometallic derivatives of platinum metals; give some examples of oxidative addition and reductive elimination! Describe some important reactions catalyzed by platinum metal complexes. *(wilkinson complex; palladium complexes; platinum complexes; isomerization, hydrogenation, carbonylation reactions; Suzuki, Heck, Sonogashira, Stille coupling reactions)*

TOPIC 2. ORGANIC CHEMISTRY

1. Aromaticity and aromatic nature - interpretation of aromaticity in cyclic compounds from 3 to 8 members. *Description and interpretation of the reactions of aromatic compounds in the nucleus and side chain. Hammett equation, aromatic electrophilic substitution, interpretation of direction rules; Nucleophilic substitution of aromatic compounds.*

2. Reactions of carbonyl compounds, in particular the formation of carbon-carbon bonds, substitution reactions in the α-position and transformations of the carbonyl group. *Reactions of carbonyl compounds - aldol condensation, Wittig reaction, hydride ion migration reactions (Cannizzaro reaction, reduction of carbonyl compounds with metal hydrides); Stable enolates, Umpolung reactions (benzoin condensation); α- Position substitution reactions (alkylation of malonate, acetic acid ester and further reactions).*

3. Stereoselective syntheses and basic concepts related to chirality and their significance in synthetic organic chemistry. *Stereochemical descriptors. Stereoselective syntheses - basic concepts related to chirality (enantiomers, enantiomeric excess, diastereomers, stereoselective and stereospecific reactions, concept of prochirality), chiral aldehydes, conformation of chiral aldehydes (using the Felkin-Ahn model), stereoselective enol chiral catalysts.*

4. Formation of carbon-carbon bonds by the reaction of nucleophilic and electrophilic centers and using organometallic reactions. *Formation of a carbon-carbon bond by the reaction of nucleophilic and electrophilic centers and using organometallic reactions. Michael reaction; alkylation and acylation of enamines; reactions starting from carbanions stabilized by an adjacent sulphur, phosphorus and silicium atoms. Formation of carbon-carbon bond on aromatic systems (Friedel-Crafts, Gatterman-Koch, Vilsmeyer reaction, Mannich reaction). Organolithium reagents; Grignard reaction; Organic reagents Cu, Cd and Zn; Pd-catalyzed coupling reactions; olefin metathesis.*

5. The use of nucleophilic substitution in organic chemistry, with particular reference to the description of mechanism types and factors influencing substitution reactions. *Application of nucleophilic substitution in organic chemistry. Interpretation of S_N1 and S_N2 processes including their main features. The Hammond principle. The effects of the substrate, the leaving group, the nucleophilic partner and the solvent on the outcome of the substitution* *reaction. Relations between mechanism and stereochemical outcome of the reactions. The neighborhood effect. Application of phase transfer catalysis in nucleophilic substitution.*

6. Mechanisms of addition and elimination reactions, empirical rules and their interpretation. Application of addition and elimination in synthetic organic chemistry. *Addition and elimination reactions. Interpretation of the Markovnikov rule; addition reactions of 1,3-butadiene; 1,3-dipolar cycloaddition. Elimination: E1, E2, E1cB mechanisms, empirical rules (Hofmann, Zaitsev elimination). Stereochemistry of the E2 reaction. Factors influencing the outcome of the elimination reaction (solvent, base, etc.) Example of abnormal eliminations (Chugayev reaction, pyrolysis of amine oxides).*

7. Electronic structure, synthesis, occurrence, role and significance of five- and six-membered oxygen and nitrogen heterocycles containing one and more heteroatoms in biochemical processes. *Electronic structure, synthesis and occurrence of five- and six-membered oxygen and nitrogen heterocycles containing one and more heteroatoms. Occurrence of heterocycles in amino acids, nucleic acids, drugs (with some examples), vitamins and coenzymes (biotin, ATP, tetrahydrofolate, lipoic acid, pyridoxal, thiamine, NAD, FMN).*

8. Significance of pericyclic reactions in organic chemistry, interpretation of pericyclic reactions based on the symmetry properties of molecular orbitals. *Interpretation of chemical bonding by the VB and MO methods. Hybridization. Hückel π-electron hypothesis. Interpretation of the electronic structure of allyl systems, butadiene and polyenes by the MO method. Interpretation of pericyclic reactions (Diels-Alder reaction, 2 + 2 addition, electrocyclization, sigmatropic rearrangements, cheletropic reactions) based on the symmetry properties of molecular orbitals.*

9. Radical reactions, photoreactions. **Formation of free radicals, their reactions and their application in synthetic organic chemistry.** *Application of free radical processes in synthetic organic chemistry (radical substitution and addition processes). Stable and unstable free radicals. The main types of photochemical reactions (homolysis, sensitization, rearrangement, isomerization, formation of neutral molecules).*

10. Structure, synthesis and reactions of amino acids, peptides, lipids, mono- and polysaccharides. *Structure and synthesis of amino acids and peptides. Structure, synthesis and reactions of monosaccharides, polysaccharides. Structure of lipids.*

Recommended reading:
Anslyn, E. V. Dougherty, D. A. *Modern Physical Organic Chemistry* (University Science Books, 2006)
Bruckner, R. *Organic Mechanisms* (Springer, 3rd ed. 2007)
Carey, F. A.; Sundberg R. J. *Advanced Organic Chemistry* A and B (Springer, 2004)
Solomons, T. W. G.; Fryhle, C. B.; Snyder, S. A. Organic chemistry (Wiley, 12th ed., 2017).

TOPIC 3: ANALYTICAL CHEMISTRY

1. Planning and implementation of sampling. Sample preparation, exploration procedures, enrichment methods. Performance characteristics of analytical methods.

Sampling aspects, dissolution, explorations, extraction, solid phase extraction, supercritical fluid extraction. Selectivity, linearity, sensitivity, distortion, precision, repeatability, reproducibility, detection effect.

2. Titrimetry. Measuring solutions, factoring, titration curves, endpoint indication, indicators, indicator error. Possibilities of determination of acids and bases. *Volumetric analysis. Factoring, titration curves, endpoint signaling, indicators, indicator error. Acid and base measuring solutions. Examples and applications: determination of strong, weak and polyvalent acids and bases, titrations in non-aqueous medium.*

3. The role of side reactions and complex formation in analytical chemistry, stability constants, apparent stability constants. Complexometric titrations. *The role of complex formation in analytical chemistry. Complex formation equilibria, stability constants, factors influencing the stability of complexes, complexometric titration methods, titration curves, operation mechanism of complexometric indicators. Examples and applications, side by side determination, camouflage.*

4. Electroanalytical methods. *Electrode types, indicator and reference electrodes. Direct potentiometry and potentiometric titration. Voltammetry: current-voltage curves, polarography, detachment potential, diffusion limit current, residual current, cyclic and inverse voltammetry, stripping technique. Amperometric titration with one and two polarizable electrodes. Conductometry, coulombmetry.*

5. Optical atomspectroscopy methods. Atomabsorption. Emission atomspectroscopy methods. *The distinction between spectroscopic methods is energy, or on the basis of characteristic movement; interpretation of simple spectra. Atomspectroscopy, atomization, excitation, ionization and error sources. The atomabsorption process and measuring devices. Flame photometry. Inductively coupled plasma optical emission method and instrumentation. Comparison of AAS and ICP-AES in terms of analytical performance characteristics.*

6. Molecular spectroscopic methods. *Fundamentals of molecular spectroscopic methods. Rotational and vibrational spectroscopy. Description of diatomic molecules, energy levels and selection rules. Principles of UV and visible spectroscopy, selection rules, vibration fine structure, practical applications, relaxation from excited states, fluorescence, phosphorescence. Characterization of the interaction with the electromagnetic radiation. Practice of visible, UV and infrared spectrophotometry. Light sources, monochromators, detectors. Spectra.*

7. Use of instrumental analytical methods (NMR, ESR, IR, MS, XRD) in the analysis of inorganic and organic compounds. Advanced 1D and 2D NMR methods for determining the structure of organic compounds. *The electron and the NMR spectroscopy. Magnetic properties of the nuclei, principle of the NMR measurement, qualitative description of a spectrum, chemical shift, spin-spin coupling, applications.*

8. Principles and applications of mass spectrometry. *General setup of mass spectrometers; formation of the mass spectrum. Ion sources (EI, CI, ESI, APCI, FAB and MALDI) and analyzer types (quadrupole, ion trap and TOF). Electrospray methods (ESI, APCI, APPI). Online LC-ESI MS. MALDI MS / MS and ESI-MS / MS methods and their application (peptides, oligosaccharides and determination of the structure of low molecular mass* *compounds). Applications of coupled techniques (ICP-MS, GC-MS, LC-MS). Comparison of experimental techniques in terms of performance and applicability.*

9. Principles, tools and practical applications of chromatographic methods. *Gas chromatographs: carrier gases, injection techniques, column types, types of stationary phases, isothermal and temperature programming in GC. Detectors. Quality identification, determination and significance of the Kováts retention index. Theory, tools and practical applications of liquid chromatographic methods. General chromatographic concepts (definition of* t_R, t'_R, K, β, α, k, N, H, R_s*). Van Deemter equation and its graphical representation. HPLC system design: pumps, injectors, columns, detectors. Stationary and mobile phases, normal and reversed phase chromatographic techniques. Gradient elution. Aspects of the proper selection of chromatographic methods.*

10. Principles, tools of the most important electrophoretic methods, and their applications. *Capillary electrophoresis, instrumentation, electrophoretic mobility, electroosmotic flow, capillary zone electrophoresis, capillary gel electrophoresis, isoelectric focusing, isotachophoresis, micellar electrokinetic chromatography.*

Literature:

Daniel C. Harris: Quantitative Chemical Analysis
Douglas A. Skoog, F. James Holler, Stanley R. Crouch: Principles of Instrumental Analysis

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TOPIC 4: PHYSICAL CHEMISTRY

1. General characterization of thermodynamic systems. *Laws of thermodynamics. State and path functions. Chemical potential and the Gibbs-Duhem equation. Functions S, U, H, A, G and their total derivatives. Maxwell relations. Gibbs' phase rule and its consequences. Relationships describing the behavior of ideal and real gases.*

2. Kinetics and mechanism of chemical reactions *General forms of rate equations of elementary reactions, their solution. Solution of the rate equations of complex reactions. Quasi-stationary and fast pre-equilibrium approximation. Chain reactions. Catalysis and inhibition. Reactive collisions: collision theory, diffusion controlled reactions, Arrhenius equation. Activated complex theory: reaction coordinate and transition state, Eyring equation.*

3. Experimental foundations of the quantum mechanical model of the atom. *Photon hypothesis and the properties of photons. Interpretation of radiation pressure and blackbody radiation. Atomic spectrum of hydrogen and its interpretation with the Bohr model. Matter-wave duality, De Broglie equation. Photoelectric effect. One-slit and two-slit experiments.*

4. Fundamentals of wave mechanics and its use in model systems. *The wave function and its properties: the principle of superposition, Born's probabilistic interpretation, normalization, ground state. Uncertainty relations. Time-dependent and stationary Schrödinger equation. Use of operators in quantum mechanics, eigenvalue equations for operators. The model systems of free motion, particle in a box, and harmonic oscillator.*

5. The description of the structure of atoms and molecules by wave mechanics. *Coulomb's law. Momentum, description of two and three dimensional circular motion in wave mechanics. Description of the electronic structure of hydrogenic atomic particles. Fundamentals of the treatment of multiparticle systems. Electron structure of the hydrogen molecule ion. Description of the electron structure of moleculues with valence bond and molecular orbital theories.*

6. Statistical thermodynamics. *Instantaneous configurations of ensembles, statistical weight. Partition function and information stored in it. Boltzmann distribution. Partition function of translation, rotation and vibration. Concept of canonical ensemble, calculation of thermodynamic functions from partition functions. Calculation of heat capacity and zero point entropy in statistical thermodynamics*.

7. Fundamentals of irreversible thermodynamics. *Entropy production, principle of minimal entropy production, general evolutionary criterion. Onsager theory of fluxes and forces, reciprocal relations. The discontinuous system. Heat transfer, thermodiffusion, thermosmosis, streaming potential, electroosmosis, Peltier effect, Seebeck effect. Affinity and the De Donder equation in reactive systems. Irreversible thermodynamics with continuous formalism.*

8. Chemistry of colloidal systems. *Surface excess energy and its consequences. Surface tension, pressure equilibrium between phases separated by a curved surface. Liquid-liquid interface, solid-liquid interface. Characteristics of dispersed systems, distribution, morphology, degree of dispersity. Stability of colloidal systems, factors affecting stability. Double layers, electrokinetic potential, electrokinetic phenomena.*

9. Properties and investigation methods for colloidal systems. *Methods for determining the size and size distribution of colloids. Adsorption phenomena, adsorption heat, adsorption state equations, adsorption isotherms (Freundlich, Langmuir, BET), hysteresis in adsorption*. *Association colloids, micelle formation, factors influencing micelle formation, liposomes, Langmuir-Blodgett films, solubilization, macromolecular colloids, polymer solutions, random coil conformation, polyelectrolytes.*